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(54) Title: DYE SUBLIMATION THERMAL TRANSFER PAPER AND TRANSFER METHOD

(57) Abstract: An image transfer sheet is provided which comprises a support, a barrier layer, a dye sublimation ink layer and a polyester layer; wherein the image transfer sheet exhibits cold peel, warm peel and hot peel properties when transferred. A method for transferring an image to a receptor element using the image transfer sheet is also provided. More specifically, the invention relates to an image transfer sheet which can be applied to a receptor element, such as cotton or cotton/polyester blend fabrics or the like.

## DYE SUBLIMATION THERMAL TRANSFER PAPER AND TRANSFER METHOD

The content of Provisional Application U.S. Serial Number 60/156,593 on which the present application is based and benefit claimed under 35 U.S.C. § 119(e) is herein

5 incorporated by reference.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to an image transfer sheet containing a support, a  
10 barrier layer, a dye sublimation ink layer and a polyester layer, and a method for transferring an image to a receptor element using the image transfer sheet. More specifically, the present invention relates to an image transfer sheet which can be applied to a receptor element, such as cotton or cotton/polyester blend fabrics or the like.

#### 15 2. Description of the Prior Art

Textiles such as shirts (e.g., tee shirts) having a variety of designs thereon have become very popular in recent years. One technique used for decorating various textiles has been the dye sublimation printing technique. In sublimation printing, a design is printed on a paper backing sheet by conventional printing techniques using sublimation  
20 inks, and then the design is transferred to a substrate under heat and pressure. Dye sublimation printing generally results in colors which stay bright during the heat transfer process.

Attempts to use dye sublimation inks in transfer designs to be applied to 100% cotton or cotton/polyester blend fabrics have resulted in distorted and faded colors.  
25 Attempts to overcome this problem have included two-step processes wherein the fabric to be printed is pretreated with an emulsion which would be more receptive to sublimation dyes. The printed image is then transferred to the treated fabric. The two-step process prevents the average consumer from using dye sublimation printing techniques, since commercial facilities are required for the pre-treating and transferring steps.

The availability of a dye sublimation printable heat transfer sheet would allow consumers to separately purchase the fabric and pre-imaged transfer sheet and decorate the fabric at home, without the assistance of professional or commercial printing processes. Alternatively, the consumer can purchase the fabric, transfer sheet, sublimation inks and  
5 the polyester coating and create a design for decorating the fabric at home.

US Patent 4,021,591 is directed to a dry release sublimation transfer element and to a method for decorating a substrate using the transfer element. The sublimation design layer has a thickness in the range of 0.1 to 3 mils.

U.S. Patent 4,555,436 is directed to a heat transferable laminate comprising a support  
10 layer, a transfer layer, an ink design layer and an adhesive. The ink design layer is composed of conventional inks.

U.S. Patent 4,657,557 relates to sublimation transfer sheets consisting of a base coated with a sublimation ink, further coated with a heat-resistant resin. A barrier layer is not employed in the sheets.

15 U.S. Patent 4,914,079 is directed to a thermal transfer ink medium containing a support, an ink layer and an ink transfer layer. A barrier layer is not incorporated into the medium.

U.S. Patent 4,927,709 is directed to a heat transferable laminate comprising a support layer, a transfer layer, an ink design layer and an adhesive. The ink design layer is composed  
20 of conventional inks.

U.S. Patent 4,935,300 is directed to a heat transferable laminate comprising a support layer, a transfer layer, an ink design layer and an adhesive. The ink design layer is composed of conventional inks.

U.S. Patent 5,322,833 relates to a dye-donor element for use in thermal dye  
25 sublimation transfers.

U.S. Patent 5,413,841 is directed to heat activated transfer elements comprising a lower adhesive layer and an upper thermoset layer which contains an indicia layer formed from sublimation dyes. The thermosetting layers do not comprise thermally activated polymers.

U.S. Patent 5,679,461 relates to thermally sensitive transfer recording materials comprising a base sheet, an ink layer and an ink-resistant lubricating layer. A barrier layer is not present between the ink layer and the lubricating layer.

U.S. Patent 5,741,387 is directed to a lithographic printing process and transfer sheet  
5 comprising a backing sheet, a heat release layer, an ink design layer, a polymer layer and a lacquer mask layer. The ink design layer is composed of conventional inks which are described as being heat-resistant.

### SUMMARY OF THE INVENTION

10 The present invention provides, in one embodiment, a transfer sheet comprising a support, a barrier layer, an image of sublimation dyes and a polyester layer, and a method for transferring an image to a receptor element using the transfer sheet. The invention provides a medium by which heat activated sublimation dyes can penetrate and adhere to a surface not  
15 inherently capable of supporting dye sublimation inks, for example, 100% cotton fabric. This medium also provides a colorfast and waterfast environment for the printed image.

Heat-activated sublimation dyes have been successfully applied only to polyester-containing materials, such as polyester or cotton/polyester blend t-shirts. This is due to the fact that polyesters enter a secondary phase transfer stage when heated to approximately the same temperature at which a dye sublimates, thereby allowing the dye to diffuse into the  
20 polyester material. When cooled, the sublimation dye locks into the polyester material. Cotton, for example, does not enter this secondary phase transition stage, and heretofore it has not been possible to apply heat-activated sublimation dyes to 100% cotton fabrics.

The present invention solves this problem in the art by delivering a material to the receptor element which provides a medium by which heat-activated sublimation dyes can  
25 penetrate and adhere to a surface not inherently capable of imaging with dye sublimation inks. The present invention relates to an image receptor element comprising a support layer, a barrier layer, a dye sublimation imaged area and a polyester layer. One embodiment of the invention provides for a method for producing a transfer sheet, which comprises the steps of:

(i) imaging a transfer sheet with sublimation dyes, wherein said transfer sheet  
30 comprises:

a support having a first and second surface, and

a barrier layer having a first and second surface, wherein the first surface of said barrier layer is applied to the first surface of said support, and wherein a sublimation dye image is applied to the second surface of said barrier layer; and

- 5       (ii) applying a first surface of a polyester layer, having a first and second surface, to said sublimation dye image applied to the second surface of said barrier layer, provided that the polyester layer does not comprise thermosetting materials.

Another embodiment of the invention provides a method of applying an image to a receptor element, which comprises the steps of:

- 10       (i) imaging a transfer sheet with sublimation dyes, wherein said transfer sheet comprises:

a support having a first and second surface, and

- a barrier layer having a first and second surface, wherein the first surface of said barrier layer is applied to the first surface of said support, and wherein said sublimation  
15 dye image is applied to the second surface of said barrier layer;

(ii) applying a first surface of a polyester layer, having a first and second surface, to said image applied to the second surface of said barrier layer to produce a transfer sheet, provided that the polyester layer does not comprise thermosetting materials;

- (iii) positioning the second surface of said polyester layer against said receptor  
20 element;

(iv) applying heat energy to the rear surface of the transfer sheet to transfer said sublimation dye image and said polyester layer to said receptor element, wherein said sublimation dyes sublime and penetrate into said polyester layer adhered to said receptor element; and

- 25       (v) stripping said transfer sheet away from said receptor element, wherein the sublimation dye image-containing polyester layer is adhered to said receptor element.

In another embodiment of the invention, a sublimation dye image is transferred to a receptor element by the steps comprising:

- (i)       providing a transfer sheet having a front and a back surface, which  
30 comprises, in the following order, the layers

- (a) a support,
- (b) a barrier layer,
- (c) a dye sublimation ink-containing layer, and
- (d) a polyester layer, provided the polyester layer does not contain  
5 thermosetting materials;
- (ii) positioning the front surface of said transfer sheet against a receptor element;
- (iii) applying heat energy to the rear surface of the transfer sheet to transfer said sublimation dye image to said receptor element, wherein said  
10 sublimation dyes sublime and penetrate into said polyester layer adhered to said receptor element; and
- (iv) stripping said transfer sheet away from said receptor element, wherein the sublimation dye image-containing polyester layer is embedded in said receptor element.
- 15 Another embodiment of the invention provides for a transfer sheet having a first and second surface, comprising:
- (i) a support layer having a first and second surface,
- (ii) a barrier layer applied to the second surface of said support layer,
- (iii) a dye sublimation ink-containing layer applied to said barrier layer, and
- 20 (iv) a polyester layer applied to said dye sublimation ink-containing layer.

In another embodiment of the invention, there is provided a kit comprising the transfer sheet of the present invention. The kit may further comprise a receptor element, such as a cotton or cotton/polyester blend fabric. Moreover, the kit may further comprise a set of directions for transferring an image from the transfer sheet to a receptor element.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a cross-sectional view of a preferred embodiment of the transfer sheet of the present invention and the image transfer procedure.

FIGURE 2 illustrates the step of ironing the transfer element onto a tee shirt or the  
30 like.

### DETAILED DESCRIPTION OF THE INVENTION

In the method of the present invention, an image is formed on a support and barrier layer as follows: a support is coated with a barrier layer, the barrier layer providing for a cool, warm or hot peel release of the image layer after transfer and functioning as a barrier to the sublimation inks upon image marking and heat transfer. The support coated by the barrier layer is then printed, image-wise, using dye sublimation inks. Once printed, the support, barrier layer and printed image are coated with a polyester, or release layer, to form a transfer sheet. This layer may comprise any polyester material which melts within a temperature range of 60°C to 270°C, flows to a receptor element, and upon cooling adheres to the receptor element thereby providing a medium for the integration of dye sublimation inks upon heat activation.

The image from the transfer sheet is transferred to a receptor element through the application of heat energy using either a hand iron or heat press on the rear surface of the support. The transfer sheet is allowed to cool to ambient temperature, or optionally, may be cooled to a warm temperature or not cooled at all. The support and barrier layer are stripped away from the transferred image, leaving the image behind on the receptor element.

#### 20 A. The Transfer Sheet

##### 1. Support

Suitable supports include those supports disclosed in U.S. applications 09/541,083 filed March 31, 2000 and 09/557,173 filed April 21, 2000, as well as U.S. Patents 5,242,739, 5,271,990 and 5,501,902 to Kronzer et al. which are herein incorporated by reference. The support provides the material for the transfer sheet onto which an image and other layers are applied. Preferably, the support will provide a surface that will promote, or at least not adversely affect, image adhesion and image release. It is preferable that the support material be resistant to damage upon heat application at temperatures less than 275°C. An appropriate support may include but is not limited to a cellulosic nonwoven web or film, such as a smooth surface, heavyweight (approximately 24 lb.) laser printer or color copier paper stock.

or laser printer transparency (polyester) film. Preferably, the support of the present invention is a sheet of laser copier/printer paper or a polyester film base. However, highly porous supports are less preferred because they tend to absorb large amounts of the toner in copiers without providing as much release. Preferably, the support of the present invention is a  
5 cellululosic nonwoven web support, a paper support or film support comprising a polyester or polyethylene terephthalate. One example of a commercially available support is a standard sheet of laser copier/printer paper such as Microprint Laser paper from Georgia Pacific.

The particular support used is not known to be critical, so long as the support has sufficient strength for handling, copying, coating, heat transfer, and other operations  
10 associated with the present invention.

In one embodiment of the invention, the support can be usable in a laser copier or laser printer. A preferred support for this embodiment is equal to or less than approximately 4.0 mils thick.

Since this particular support is useable in a laser copier or laser printer, antistatic  
15 agents may be present. The antistatic agents may be present in the form of a coating on the back surface of the support as an additional layer. The back surface of the support is the surface that is not previously coated with the release layer, barrier layer, etc.

When the antistatic agent is applied as a coating onto the back surface of the support, the coating will help eliminate copier or printer jamming by preventing the  
20 electrostatic adhesion of the paper base to the copier drum of laser and electrostatic copiers and printers. Antistatic agents, or "antistats" are generally, but not necessarily, conductive polymers that promote the flow of charge away from the paper. Antistats can also be "humectants" that modulate the level of moisture in a paper coating that affects the build up of charge. Antistats are commonly charged tallow ammonium compounds and  
25 complexes, but also can be complexed organometallics. Antistats may also be charged polymers that have a similar charge polarity as the copier/printer drum; whereby the like charge repulsion helps prevent jamming.

Antistatic agents include, by way of illustration, derivatives of propylene glycol, ethylene oxide-propylene oxide block copolymers, organometallic complexes such as



titanium dimethylacrylate oxyacetate, polyoxyethylene oxide-polyoxypropylene oxide copolymers and derivatives of cholic acid.

- More specifically, commonly used antistats include those listed in the Handbook of Paint and Coating Raw Materials, such as t-Butylaminoethyl methacrylate; Capryl
- 5 hydroxyethyl imidazoline; Cetethyl morpholinium ethosulfate; Cocoyl hydroxyethyl imidazoline Di(butyl, methyl pyrophosphato) ethylenetitanate di(dioctyl, hydrogen phosphite); Dicyclo (dioctyl)pyrophosphato; titanate; Di (dioctylphosphato) ethylene titanate; Dimethyl diallyl ammonium chloride; Distearylmonium chloride; N,N'-Ethylene bis-ricinoleamide; Glyceryl mono/dioleate; Glyceryl oleate; Glyceryl stearate;
  - 10 Heptadecenyl hydroxyethyl imidazoline; Hexyl phosphate; N( $\beta$ -Hydroxyethyl)ricinoleamide; N-(2-Hydroxypropyl) benzenesulfonamide; Isopropyl 4-aminobenzenesulfonyl di(dodecylbenzenesulfonyl)titanate; Isopropyl dimethacryl isostearoyl titanate; isopropyltri(dioctylphosphato) titanate; Isopropyl tri(dioctylpyrophosphato)titanate; Isopropyl tri(N ethylaminoethylamino) titanate; (3-
  - 15 Lauramidopropyl) trimethyl ammonium methyl sulfate; Nonyl nonoxynol-15; Oleyl hydroxyethylimidazoline; Palmitic/stearic acid mono/diglycerides; PCA; PEG-36 castor oil; PEG-10 cocamine; PEG-2 laurate; PEG-2; tallowamine; PEG-5 tallowamine; PEG-15 tallowamine; PEG-20 tallowamine; Poloxamer 101; Poloxamer 108; Poloxamer 123; Poloxamer 124; Poloxamer 181; Poloxamer 182; Polaxamer 184; Poloxamer 185;
  - 20 Poloxamer 188; Poloxamer 217; Poloxamer 231; Poloxamer 234; Poloxamer 235; Poloxamer 237; Poloxamer 282; Poloxamer 288; Poloxamer 331; Polaxamer 333; Poloxamer 334; Poloxamer 335; Poloxamer 338; Poloxamer 401; Poloxamer 402; Poloxamer 403; Poloxamer 407; Poloxamine 304; Poloxamine 701; Poloxamine 704; Polaxamine 901; Poloxamine 904; Poloxamine 908; Poloxamine 1107; Poloxamine 1307;
  - 25 Polyamide/epichlorohydrin polymer; Polyglyceryl-10 tetraoleate; Propylene glycol laurate; Propylene glycol myristate; PVM/MA copolymer; polyether; Quaternium-18; Slearamidopropyl dimethyl- $\beta$ -hydroxyethyl ammonium dihydrogen phosphate; Stearamidopropyl dimethyl-2-hydroxyethyl ammonium nitrate; Sulfated peanut oil; Tetra (2, diallyloxymethyl-1 butoxy titanium di (di-tridecyl) phosphite; Tetrahydroxypropyl
  - 30 ethylenediamine; Tetraisopropyl di (dioctylphosphito) titanate; Tetraoctyloxytitanium di

(ditridecylphosphite); Titanium di (butyl, octyl pyrophosphate) di (dioctyl, hydrogen phosphite) oxyacetate; Titanium di (cumylphenylate) oxyacetate; Titanium di (dioctylpyrophosphate) oxyacetate; Titanium dimethacrylate oxyacetate.

Preferably, Marklear AFL-23 or Markstat AL-14, polyethers available from  
5 Whitco Industries, are used as an antistatic agents.

The antistatic coating may be applied on the back surface of the support by, for example, spreading a solution comprising an antistatic agent (i.e., with a metering rod) onto the back surface of the support and then drying the support. The present invention may use the antistatic coating disclosed in U.S. application 09/541,083 filed March 31 by  
10 Williams et al.

An example of a preferred support of the present invention is Georgia Pacific brand Microprint Laser Paper. However, any commercially available laser copier/printer paper may be used as the support in the present invention.

## 15 2. Barrier Layer

Suitable barrier layers include the barrier layers disclosed in U.S. applications 09/541,083 filed March 31, 2000 and 09/557,173 filed April 21, 2000, which are herein incorporated by reference. The barrier layer is coated on the support and assists in releasing the image layer. The barrier layer can be any material which will provide a cool, warm or hot  
20 peel release of the image layer after transfer, and which will function as a support barrier to the sublimation inks upon image marking and heat transfer.

In one embodiment, the barrier layer comprises a polymer dispersion. For example, the polymer dispersion may comprise one or more of the components selected from the group consisting of polyacrylates, styrene-butadiene copolymers, ethylene-vinyl acetate  
25 copolymers, nitrile rubbers, poly(vinylchloride), poly(vinylacetate) and ethylene-acrylate copolymers. Preferably, the polymer dispersion comprises polyvinyl acetate dibutyl maleate copolymer.

In another embodiment, the barrier layer has a melting point of at least 65°C and comprising (i) particles of a thermoplastic polymer having dimensions of about 1 to about 50  
30 micrometers, from about 10 to about 50 weight percent of a film-forming binder, based on

the weight of the thermoplastic polymer, and optionally from about 0.2 to about 10 weight percent of a fluid viscosity modifier, based on the weight of the thermoplastic polymer, (ii) about 15 to about 80 percent by weight of a film-forming binder selected from the group consisting of ethylene-acrylic acid copolymers, polyolefins, and waxes and from about 85 to about 20 percent by weight of a powdered thermoplastic polymer selected from the group consisting of polyolefins, polyesters, polyamides, waxes, epoxy polymers, ethylene-acrylic acid copolymers, and ethylene-vinyl acetate copolymers, wherein each of said film-forming binder and said powdered thermoplastic polymer melts in the range of from about 65°C to about 180 degrees Celsius and the powdered thermoplastic polymer consists of particles of about 1 to about 50 micrometers, (iii) a film forming binder selected from the group consisting of ethylene-acrylic acid copolymers having particles of about 1 to about 50 micrometers, polyolefins, and waxes and which melts in the range of from about 65°C to about 180 degrees Celsius, (iv) a thermoplastic polymer having particles of about 1 to about 50 micrometers selected from the group consisting of polyolefins, polyesters, and ethylene-vinyl acetate copolymers and which melts in the range of from about 65 to about 180 degrees Celsius or, (v) a thermoplastic polymer having particles of about 1 to about 50 micrometers selected from the group consisting of polyolefins, polyesters, and ethylene-vinyl acetate copolymers, ethylene-methacrylic acid copolymers, and ethylene-acrylic acid copolymers and which melts in the range of from about 65 to about 180 degrees Celsius; wherein said transfer layer is capable of transferring and adhering developed image and non-image areas from said front surface of said support upon the application of heat energy to the rear surface of the support, said transfer layer strips from said front surface of the support by liquefying and releasing from said support when heated, said liquefied transfer layer providing adherence to a receptor element by flowing onto said receptor element and solidifying thereon, said adherence does not require an external surface adhesive layer.

In another embodiment, the barrier layer may comprise a polymer selected from the group consisting of a thermosetting polymer, an ultraviolet curable polymer, and combinations thereof, or the barrier layer may comprise acetone, 2-propanol, and polymethyl methacrylate. The thermosetting polymer is preferably selected from the group consisting of thermosetting acrylic polymers and blends; thermosetting polyurethanes, block polyurethanes

and aromatic-functional urethanes; thermosetting polyester polymers and co-polymer systems; aromatic-functional vinyl polymers and polymer blends; and thermosetting epoxy resins.

Materials that fall into the class of thermosetting polymers should function as  
5 either a cool, hot or warm peel barrier layer of the present invention. Thermosetting polymers are both chemically and physically distinct from thermoplastic polymers, which, among other properties, flow upon the addition of heat energy. The fact that the thermosetting material polymerizes to form a layer which cannot be re-melted and flow with heat energy imparts both a hot and cold peel release property. That is, the  
10 thermosetting material of the barrier layer of the present invention will not undergo a temperature dependent physical state change which can produce, among other properties, a tack that could provide a physical adherence of the release layer to the support base.

Thermosetting materials include thermosetting acrylic polymers and blends, such as hydroxyl-functional acrylic polymers and carboxy-functional acrylic polymers and  
15 vinyl acrylic polymer blends; thermosetting polyurethanes, block polyurethanes and aromatic-functional urethanes; thermosetting polyester polymers and co-polymer systems such as neopentyl glycol isophthalic polyester resins, dibromoneopentyl glycol polyester resins and vinyl ester resins; aromatic-functional vinyl polymers and polymer blends; and thermosetting epoxy resins, in particular, epoxy novolac resins. Generally, the  
20 thermosetting polymer system(s) must undergo crosslinking reaction(s) over a range of temperatures from ambient (e.g. 190°) to 250°C over a period of less than thirty (30) minutes.

Coating weights may range from one(1) gram per meter square to 20 grams per meter square, preferably from 1 g/m<sup>2</sup> to 15 g/m<sup>2</sup>, most preferably 1 g/m<sup>2</sup> to 8 g/m<sup>2</sup>.

25 The Barrier Layer also may optionally include an effective amount of a release-enhancing additive for assisting in release of the release layer from the barrier during peeling, such as a divalent metal ion salt of a fatty acid, a polyethylene glycol, or a mixture thereof. The release-enhancing additive may be present in an amount of from 0.1 to 40% by weight, preferably 0.1 to 20% by weight, most preferably 0.1 to 10% by weight.

For example, the release-enhancing additive may be calcium stearate, a polyethylene glycol having a molecular weight of from about 2,000 to about 100,000, or a mixture thereof. For a description of suitable thermosetting polymers, see pages 10 to 13 of Polymer Chemistry, an Introduction, Malcolm P. Stevens, 1990; and pages 113 and 299 of Textbook of Polymer Science, Fred W. Billmeyer, Jr., 1962.

Preferably, the barrier layer is any vinyl acetate with a Tg in the range of from -10°C to 100°C. Alternatively, the Tg may be in the range of from 0°C to 100°C. EVERFLEX G, with a Tg of about -7°, may be used as a preferred embodiment.

Ultraviolet curable/setting materials may be used as the barrier layer of the present invention. UV setting materials can be divided into two classes based upon the mechanism by which they set. The first class of ultraviolet curing/setting materials set via a cationic mechanism while the second class sets via a free radical mechanism. It is important to note, however, that a number of ultraviolet curing systems incorporate both classes into a single formulation, typically termed a hybrid resin system. In one embodiment of the present invention, the ultraviolet curing system, especially when comprising cationic systems, may incorporate thermosetting polymers, thereby resulting in systems that typically are cured initially by ultraviolet activation, then further cured by exposure to a heat source. In such an embodiment, the final coated surface has the best properties of both thermosetting and ultraviolet setting systems. As a consequence of such multiple pathways to create the final cured coating, the ultraviolet setting compounds to be listed herein may be activated by any combination of the mechanisms described herein.

Furthermore, the thermosetting or UV curable barrier layer of the present invention may be combined with at least one vinyl acetate polymer. One of ordinary skill in the art would recognize the appropriate mechanism or mechanisms by which to activate a specific formulation of ultraviolet curing compounds and formulations that include both ultraviolet curing compounds and thermosetting compounds.

Typical formulations of ultraviolet curable systems are composed of primary resins, which provide the major film-forming properties; modifying resins, which modify the film properties to meet specifications for the application in which it is to be used; additives, which provide or enhance specific properties of the film; and photoinitiators

which, when exposed to an ultraviolet radiation source, begin the cross-linking reaction that cures the system. The UV curable polymers of the present invention are typically cured at  $<50 \text{ mJ/cm}^2$  with a mercury vapor ultraviolet lamp.

Primary and modifying resins are discussed as a single class as they often cross  
5 over from one application to the next. These ultraviolet curable resins include, but are not limited to monomers and oligomers. Monomers such as monofunctional monomers including acrylates, methacrylates, and ethylacrylates; difunctional monomers including various diacrylates and dimethacrylates, especially tripropylene glycol diacrylate, bisphenol A diacrylates and ethoxylated bisphenol A dimethacrylates; trifunctional  
10 monomers including various triacrylates and trimethacrylates, especially trimethylolpropane ethoxy triacrylate and trimethyl propane triacrylates; higher functionality monomers including tetra- and pentaacrylates and pentaacrylate esters; aliphatic and aromatic acrylates; aromatic urethane acrylates; metallic acrylates; water dispersible monomers such as, for example, 2(2-ethoxyethoxy) ethylacrylate and  
15 polyethylene glycol diacrylates; adhesion promoting monomers such as various acrylate esters and methacrylate esters; pigment dispersing monomers; and scorch retarding monomers.

Oligomers such as aliphatic urethane acrylates; aliphatic urethane diacrylates; aliphatic urethane triacrylates; hexafunctional aliphatic urethane acrylates; hexafunctional  
20 aromatic urethane acrylates; trifunctional aromatic urethane acrylates, aromatic urethane acrylates; urethane methacrylates; epoxy acrylates; epoxy methacrylates; polybutadiene dimethylacrylates; diacrylates of bisphenol-A epoxy resins; modified bisphenol-A epoxy acrylate resins; novolac epoxy acrylates; modified epoxy acrylates, partially acrylated bisphenol-A epoxy resins; bisphenol-A epoxy diacrylates; polyester resins including  
25 chlorinated polyester resins, modified polyester resins, polyester methacrylates, acrylated polyesters, modified polyester acrylates, modified polyester hexaacrylates, polyester tetraacrylates, and hexafunctional polyester acrylates; cycloaliphatic epoxides, especially 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexane carboxylate; modified cycloaliphatic epoxides, especially acrylate modified cycloaliphatic

epoxides containing both acrylate and epoxy functionalities; aliphatic polyols; partially acrylated bisphenol-A epoxy resins; and cycloaliphatic diepoxides.

Photoinitiators for the ultraviolet curable systems include, but are not limited to alpha hydroxy ketone; benzil dimethyl ketal; benzoin normal butyl ethers; benzophenone; 5 modified benzophenones; polymeric hydroxy ketones; trimethylbenzophenone blends; sulfonium, iodonium, ferrocenium or diazonium salts, especially cyclic 1,2-propylene carbonate *bis-p*-diphenylsulfoniumphenylsulfide hexafluorophosphate, and diphenylsulfonium hexafluorophosphate; peroxides; cobaloximes and related cobalt (II) complexes; and organic photoinitiators such as, for example, 2,2-diethoxyacetophenone, 10 ethyl 4-(dimethylamino)benzoate, methyldiethanolamine, isopropylthioxanthone, and especially 2-hydroxy-2-methyl-1-phenyl-1-propanone.

Additives that may be used in the above-described ultraviolet curable systems include, but are not limited to photoinitiator activators; slip agents; leveling agents; wetting agents; adhesion promoters; anti-absorption agents; anti-foaming agents, 15 especially mixtures of foam destroying polymers and polysiloxanes; accelerators; pigment dispersion aids; anti-blocking agents; anti-caking agents; anti-slip agents; anti-skinning agents; anti-static agents; anti-stripping agents; binders; curing agents; crosslinking agents; deaerators; diluents; dispersants; dryers; emulsifiers; fillers; flattening agents; flow control agents; gloss agents; hardeners; lubricants; mar resistance aids; whiteners; plasticizers; 20 solvents; stabilizers; surfactants; viscosity modifiers; UV stabilizers; UV absorbers; and water repellants. The barrier layer of the present invention may also comprise the cross-linking polymers of US 5,603,996 to Overcash et al. Specifically, see Overcash et al. at cols. 5-8.

The barrier layer may comprise an acrylic polymer, or resin, as a cross-linkable 25 polymer. Additional cross-linkable acrylic polymers include MICHEM COAT 50A, made by Michelman, Inc., and RHOPLEX.RTM. P-376 and RHOPLEX.RTM. B-15, made by Rohm and Haas. In addition, styrene-butadiene resins, or polymers, ("SBR") are suitable as cross-linkable polymers in the barrier coating composition, including such SBR's as MICHEM COAT 50H, made by Michelman, Inc., and Latex PB 6692NA made by Dow 30 Chemical. Blends and/or copolymers of cross-linkable polymers may also be used. Other

cross-linkable polymers, such as polyurethane polymers and various fluorochemical polymers (e.g., 3B ZONYL.RTM. 7040 made by Du Pont), may also provide the necessary barrier properties.

A more specific listing of polymers that may be used as cross-linkable polymers  
5 includes, but is not limited to:

polymers and copolymers of poly(dienes) such as poly(butadiene), poly(isoprene), and poly(1-pentenylene);

poly(acrylics) such as poly(benzyl acrylate), poly(butyl acrylate) (s), poly(2-cyanobutyl acrylate), poly(2-ethoxyethyl acrylate), poly(ethyl acrylate), poly(2-ethylhexyl  
10 acrylate), poly(fluoromethyl acrylate), poly(5,5,6,6,7,7,7-heptafluoro-3-oxaheptyl acrylate), poly(heptafluoro-2-propyl acrylate), poly(heptyl acrylate), poly(hexyl acrylate), poly(isobornyl acrylate), poly(isopropyl acrylate), poly(3-methoxybutyl acrylate), poly(methyl acrylate), poly(nonyl acrylate), poly(octyl acrylate), poly(propyl acrylate), and poly(p-tolyl acrylate);

15 poly(acrylamides) such as poly(acrylamide), poly(N-butylacrylamide), poly(N,N-dibutylacrylamide), poly(N-dodecylacrylamide), and poly(morpholylacrylamide);

poly(methacrylic acids) and poly(methacrylic acid esters) such as poly(benzyl methacrylate), poly(octyl methacrylate), poly(butyl methacrylate), poly(2-chloroethyl methacrylate), poly(2-cyanoethyl methacrylate), poly(dodecyl methacrylate), poly(2-  
20 ethylhexyl methacrylate), poly(ethyl methacrylate), poly(1,1,1-trifluoro-2-propyl methacrylate), poly(hexyl methacrylate), poly(2-hydroxyethyl methacrylate), poly(2-hydropropyl methacrylate), poly(isopropyl methacrylate), poly(methacrylic acid), poly(methyl methacrylate) in various forms such as, atactic, isotactic, syndiotactic, and heterotactic; and poly(propyl methacrylate);

25 poly(methacrylamides) such as poly(4-carboxy phenylmethacrylamide);

other alpha-and beta-substituted poly(acrylics) and poly(methacrylics) such as poly(butyl chloracrylate), poly(ethyl ethoxycarbonylmethacrylate), poly(methyl fluoroacrylate), and poly(methyl phenylacrylate);

poly(vinyl ethers) such as poly(butoxyethylene), poly(ethoxyethylene),  
30 poly(ethylthioethylene),



(dodecafluorobutoxyethylene), poly(2,2,2-trifluoroethoxytrifluoroethylene), poly(hexyloxyethylene), poly(methoxyethylene), and poly(2-methoxypropylene);

poly(vinyl halides) and poly(vinyl nitriles) such as poly(acrylonitrile), poly(1,1-dichloroethylene), poly(chlorotrifluoroethylene), poly(1,1-dichloro-2-fluoroethylene),  
5 poly(1,1-difluoroethylene), poly(methacrylonitrile), poly(vinyl chloride), and poly(vinylidene chloride);

poly(vinyl esters) such as poly(vinyl acetate), poly(benzoyloxyethylene), poly(4-butyryloxybenzoyloxyethylene), poly(4-ethylbenzoyloxyethylene), poly[(trifluoroacetoxy)ethylene], poly[(heptafluorobutyryloxy)ethylene],  
10 poly(formyloxyethylene), poly[(2-methoxybenzoyloxy)ethylene], poly(pivaloyloxyethylene), and poly(propionyloxyethylene);

poly(styrenes) such as, poly(4-acetylstyrene), poly[3-(4-biphenyl)styrene], poly(4-[(2-butoxyethoxy) methyl]styrene), poly(4-butoxymethyl styrene), poly(4-butoxystyrene), poly(4-butylstyrene), poly(4-chloro-2-methylstyrene), poly(2-chlorostyrene), poly(2,4-dichlorostyrene), poly(2-ethoxymethyl styrene), poly(4-ethoxystyrene), poly(3-ethylstyrene), poly(4-fluorostyrene), poly(perfluorostyrene), poly(4-hexylstyrene), poly [4-(2-hydroxyethoxymethyl)styrene], poly [4-(1-hydroxy-1-methylpropyl)styrene], poly(2-methoxymethylstyrene), poly(2-methoxystyrene), poly(alpha-methylstyrene), poly(2-methylstyrene), poly(4-methoxystyrene), poly(4-octanoylstyrene), poly(4-phenoxy styrene), poly(4-phenylstyrene), poly(4-propoxystyrene),  
15 20 and poly(styrene);

poly(oxides) such as poly(ethylene oxides), poly(tetrahydrofuran), poly(oxetanes), poly(oxybutadiene), poly[oxychloromethyl]ethylene], poly(oxy-2-hydroxytrimethyleneoxy-1,4-phenylenemethylene-1, 4-phenylene), poly(oxy-2,6-dimethoxy-1,4-phenylene), and poly(oxy-1,3-phenylene);  
25

poly(carbonates) such as polycarbonate of Bisphenol A, and poly[oxy-carbonyloxy-4,6-dimethyl]-1,2-phenylenemethylene-3,5-dimethyl-1,2-phenylene];

poly(esters) such as poly(ethylene terephthalate), poly[(1,2-diethoxycarbonyl)ethylene], poly[(1,2-dimethoxycarbonyl)ethylene], poly(oxy-2-butenyleneoxysebacoyl), poly[di(oxyethylene)oxyadipoyl], poly(oxyethyleneoxycarbonyl)-  
30

1,4-cyclohexylenecarbonyl), poly(oxyethyleneoxyisophthaloyl),  
 poly[di(oxyethylene)oxyoxalyl], poly[di(oxyethylene)oxysuccinyl],  
 poly(oxyethyleneoxyterephthaloyl), poly(oxy-1,4-phenyleneisopropylidene-1,4-phenylene  
 oxysebacoyl), and poly(oxy-1,3-phenyleneoxyisophthaloyl);

5 poly(anhydrides) such as poly(oxycarbonyl-1,4-phenylenemethylene-1,4-phenyl  
 enecarbonyl), and poly(oxyisophthaloyl);

poly(urethanes) such as

poly(oxycarbonyliminohexamethyleneiminocarbonyloxydecamethylene),

poly(oxyethyleneoxycarbonyliminiohexamethyleneiminocarbonyl),

10 poly(oxyethyleneoxycarbonylimino-1,4-phenylenetrimethylene-1,4-phenyleneim  
 inocarbonyl), poly(oxydodecamethyleneoxycarbonyliminododecamethyleneiminocarbonyl),  
 and poly(oxytetramethyleneoxycarbonylimino-1,4-phenylenemethylene-1,4-  
 phenyleneiminocarbonyl);

poly(siloxanes) such as, poly(dimethylsiloxane), poly[oxy(methyl)phenylsilylene],

15 and poly(oxydiphenylsilylene-1,3-phenylene);

poly(sulfones) and poly(sulfonamides) such as poly[oxycarbonyl di(oxy-1,4-  
 phenylene)sulfonyl-1,4-phenyleneoxy-1,4-phenylene], poly[oxy-1,4-phenylenesulfinyl-  
 1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene], poly(oxy-1,4-  
 phenylenesulfonyl-1,4-phenylene), and poly(sulfonyl-1,3-cyclohexylene);

20 poly(amides) such as nylon-6, nylon-6,6, nylon-3, nylon-4,6, nylon-5,6, nylon-6,3,  
 nylon-6,2, nylon-6,12, and nylon-12;

poly(imines) such as poly(acetylminoethylene), and poly(valeryl iminoethylene);

poly(benzimidazoles) such as poly(2,6-benzimidazolediy-6,2-  
 benzimidazolediyloctamethylene);

25 carbohydrates such as amylose triacetate, cellulose triacetate, cellulose  
 tridecanoate, ethyl cellulose, and methylcellulose;

and polymer mixtures and copolymers thereof such as poly(acrylonitrile-co-  
 styrene) with poly( $\epsilon$ -caprolactone), or poly(ethyl methacrylate), or poly(methyl  
 methacrylate);

30 poly (acrylonitrile-co-vinylidene chloride) with poly(hexamethylene terephthalate);

poly (allyl alcohol-co-styrene) with poly(butylene adipate), or poly(butylene sebacate); poly(n-amyl methacrylate) with poly(vinyl chloride);

bisphenol A polycarbonate with poly(e-caprolactone), or poly(ethylene adipate), or poly(ethylene terephthalate), or novolac resin;

5 poly(butadiene) with poly(isoprene);

poly(butadiene-co-styrene) with glycerol ester of hydrogenated rosin;

poly(butyl acrylate) with poly(chlorinated ethylene), or poly(vinyl chloride);

poly(butyl acrylate-co-methyl methacrylate) with poly(vinyl chloride);

poly(butyl methacrylate) with poly(vinyl chloride);

10 poly(butylene terephthalate) with poly(ethylene terephthalate), or poly(vinyl acetate-co-vinylidene chloride);

poly(e-caprolactone) with poly(chlorostyrene), or poly(vinyl acetate-co-vinylidene chloride);

cellulose acetate with poly(vinylidene chloride-co-styrene);

15 cellulose acetate-butyrate with poly(ethylene-co-vinyl acetate);

poly(chlorinated ethylene) with poly(methyl methacrylate);

poly(chlorinated vinyl chloride) with poly(n-butyl methacrylate), or poly(ethyl methacrylate), or poly(valerolactone);

poly(chloroprene) with poly(ethylene-co-methyl acrylate);

20 poly(2,6-dimethyl-1,4-phenylene oxide) with poly(a-methylstyrene-co-styrene styrene), or poly(styrene);

poly(ethyl acrylate) with poly(vinyl chloride-co-vinylidene chloride), or poly(vinyl chloride);

poly(ethyl methacrylate) with poly(vinyl chloride);

25 poly(ethylene oxide) with poly(methyl methacrylate);

poly(styrene) with poly(vinyl methyl ether); and

poly(valerolactone) with poly(vinyl acetate-co-vinylidene chloride).

Another suitable barrier layer may be the release layer of U.S. Patent 5,798,179 to Kronzer. The barrier layer may be composed of a thermoplastic polymer having  
30 essentially no tack at transfer temperatures (e.g., 60-220°C.), a solubility parameter of at

least about  $19 \text{ (Mpa)}^{1/2}$ , and a glass transition temperature of at least about  $0^{\circ}\text{C}$ . As used herein, the phrase "having essentially no tack at transfer temperatures" means that the barrier layer does not stick to the polyester layer to an extent sufficient to adversely affect the quality of the transferred image. By way of illustration, the thermoplastic polymer may  
5 be a hard acrylic polymer or poly(vinyl acetate). For example, the thermoplastic polymer may have a glass transition temperature ( $T_g$ ) of at least about  $25^{\circ}\text{C}$ . As another example, the  $T_g$  may be in a range of from about  $25^{\circ}\text{C}$  to about  $100^{\circ}\text{C}$ . The barrier layer also may include an effective amount of a release-enhancing additive, such as a divalent metal ion salt of a fatty acid, a polyethylene glycol, or a mixture thereof. For example, the release-  
10 enhancing additive may be calcium stearate, a polyethylene glycol having a molecular weight of from about 2,000 to about 100,000, or a mixture thereof.

Additionally, there are no primary or secondary changes of state upon heating that would alter the physical characteristics (such as, for example, surface residue) upon transfer. The barrier layer of the present invention preferably transfers no residue to the  
15 transferred image. The barrier layer of the present invention allows efficient conduction of heat to the polyester layer and sublimation inks, the barrier layer preferably provides a water barrier that helps prevent penetration of the support.

In a preferred embodiment of the invention, the barrier layer is a vinyl acetate polymer. In another embodiment of the present invention, the barrier layer contains a  
20 polyester resin such as polymethyl methacrylate (PMMA) in a molecular weight range of from 15,000 to 120,000 Daltons.

The barrier layer may possess hot, warm and cold peel properties, such as when EVERFLEX G is used as part of the barrier layer. That is, after heat is applied to the transfer sheet and the image is transferred to the receptor, the transfer sheet may be peeled away from  
25 the receptor immediately after ironing (hot peel), before it is allowed to cool (i.e., warm peel), or alternatively, the transfer sheet is allowed to cool before it is peeled away from the receptor (i.e., cold peel).

By way of example, the barrier layer may comprise the following polymers which have suitable glass transition temperatures as disclosed in U.S. Patent No. 5,798,179 to  
30 Kronzer:

Polymer Type	Product Identification
Polyacrylates	Hycar ® 26083, 26084, 26120, 26104, 26106, 26322, B.F. Goodrich Company, Cleveland, Ohio Rhoplex ® HA-8, HA-12, NW-1715, Rohm and Haas Company, Philadelphia, Pennsylvania Carboset ® XL-52, B.F. Goodrich Company, Cleveland, Ohio
Styrene-butadiene copolymers	Butofan ® 4264, BASF Corporation, Samia, Ontario, Canada DL-219, DL-283, Dow Chemical Company, Midland, Michigan
Ethylene-vinyl acetate copolymers	Dur-O-Set ® E-666, E-646, E-669, National Starch & Chemical Co., Bridgewater, New Jersey
Nitrile rubbers	Hycar ® 1572, 1577, 1570 x 55, B.F. Goodrich Company, Cleveland, Ohio
Poly(vinyl chloride)	Vycar ® 352, B.F. Goodrich Company, Cleveland, Ohio
Poly (vinyl acetate)	Vinac XX-210, Air Products and Chemicals, Inc., Napierville, Illinois
Ethylene-acrylate copolymers	Michem ® Prime, 4990, Michelman, Inc., Cincinnati, Ohio Adcote 56220, Morton Thiokol, Inc., Chicago, Illinois

An additional embodiment of the barrier layer of the present invention is 100 parts (by weight) Polyester Resin (Polylite 32-737; Reichhold, Inc.). The polyester coating is applied with a dry coat weight of from 1 to 20 g/m<sup>2</sup>, preferably 1-15 g/m<sup>2</sup> and most preferably 1-8 g/m<sup>2</sup>. Coating methods include gravure, metered rod, air knife, cascade, etc. Coatings are cured by exposure to thermal energy that ranges from 30°C to 250°C, preferably 70°C to 200°C, and most preferably 120° to 170°C. Curing times range from 10 seconds to 20 minutes, preferably from 1 minute to 18 minutes, most preferably from 8 minutes to 15 minutes.

### 3. Dye Sublimation Ink Layer

Suitable dye sublimation inks include those disclosed in U.S. patents 5,919,609, 5,919,610, 5,888,253, 5,698,364, 5,910,812 and 5,863,860, which are herein incorporated by reference.

The image-wise marking using sublimation dyes can be achieved using any conventional mechanism by which color images (e.g. inks or dyes) are applied to a substrate.

For example, the marking can be either from electronic reproduction devices, such as electrostatic printers including but not limited to laser printers or laser copiers (color or monochromatic) wherein the sublimation ink pigments are granules dispersed in a carrier, ink-jet printers wherein the sublimation dyes are dispersed in a solvent, dye sublimation  
5 printers and the like, or the imaging can be accomplished through conventional printing processes, such as sheet fed offset, web offset, gravure, flexographic or screen printing.

Generally, dye sublimation inks are made from a class of dyes known as Acid, Vat, Pigment, disperse, Direct and Reactive Dyes. Typically, Disperse and Direct Dyes are commonly found in sublimation formulations. These dyes are derived from the chemical  
10 class of organic systems known as azo anthroquinone and phthalocyanine dye systems. Preferred sublimation dyes are a four to eight color dye sublimation ink sets. Further, the present invention may be practiced using craft-type marking agents comprising sublimation dyes, such as, for example, markers crayons, paints or pens. A preferred dye sublimation layer is approximately 0.1 to 3.5 mils thick, preferably 0.5 to 3.0 mils.

15

#### 4. Polyester Layer

Suitable polyester layers include those release layers disclosed in U.S. applications 09/541,083 filed March 31, 2000 and 09/557,173 filed April 21, 2000, which are herein incorporated by reference. The polyester layer is formed on the dye sublimation ink layer  
20 and comprises any polyester material or combination of polyester materials which melts within a temperature range of from about 60°C to about 270°C, flows to a receptor element, and adheres to the receptor element to provide a medium for integration of dye sublimation inks upon heat activation. The polyester layer further serves as a release layer which facilitates the transfer of the image from the support and barrier layers to the receptor. The  
25 polyester layer transfers with the image from the support and barrier layers to the desired receptor. Therefore, the polyester layer should provide the properties to effectively transfer the polyester layer and the image from the dye sublimation ink layer, as well as any additional layers thereon if necessary. Further, the polyester layer should also provide for adhesion of the polyester layer and dye sublimation ink layer to the receptor without the  
30 requirement of a separate surface adhesive layer.

The polyester layer does not contain thermosetting materials, such as thermosetting polymers. Thermosetting polymers are both chemically and physically distinct from thermoplastic polymers, which, among other properties, flow upon the addition of heat energy. The fact that the thermosetting material polymerizes to form a layer which cannot  
5 be re-melted and flow with heat energy imparts both a hot and cold peel release property. That is, the thermosetting material will not undergo a temperature dependent physical state change which can produce a tack, among other properties.

Thermosetting materials include thermosetting acrylic polymers and blends, such as hydroxyl-functional acrylic polymers and carboxy-functional acrylic polymers and  
10 vinyl acrylic polymer blends; thermosetting polyurethanes, block polyurethanes and aromatic-functional urethanes; thermosetting polyester polymers and co-polymer systems such as neopentyl glycol isophthalic polyester resins, dibromoneopentyl glycol polyester resins and vinyl ester resins; aromatic-functional vinyl polymers and polymer blends; and thermosetting epoxy resins, in particular, epoxy novolac resins. Generally, the  
15 thermosetting polymer system(s) must undergo crosslinking reaction(s) over a range of temperatures from ambient (e.g. 190°) to 250°C over a period of less than thirty (30) minutes.

In one embodiment, the polyester layer comprises a (a) polyester or polyester/copolymer blend or acrylic dispersion, (b) an elastomeric emulsion, (c) a water  
20 repellant and (d) a plasticizer, wherein the polyester or polyester/polymer blend melts in the range of about 60°C to 270°C. In an preferred embodiment, the acrylic dispersion is an ethylene acrylic acid dispersion, the water repellant is a polyurethane dispersion and the plasticizer is a polyethylene glycol. More preferably, the ethylene acrylic acid dispersion melts in the range of from about 65°C to about 180°C. By way of example, the ethylene  
25 acrylic acid dispersion may be present in an amount of from 46 to 90 parts by weight; the elastomeric emulsion may be present in an amount of from 1 to 45 parts by weight; the polyurethane dispersion may present in an amount of from 1 to 7 parts by weight; and the polyethylene glycol may be present in an amount of from 1 to 8 parts by weight.

In one embodiment, the polyester layer has a melting point of at least 65°C and  
30 comprises (i) particles of a thermoplastic polymer having dimensions of about 1 to about 50

micrometers, from about 10 to about 50 weight percent of a film-forming binder, based on the weight of the thermoplastic polymer, and optionally from about 0.2 to about 10 weight percent of a viscosity modifier, based on the weight of the thermoplastic polymer, (ii) about 15 to about 80 percent by weight of a film-forming binder selected from the group consisting of ethylene-acrylic acid copolymers, polyolefins, and waxes and from about 85 to about 20 percent by weight of a powdered thermoplastic polymer selected from the group consisting of polyolefins, polyesters, polyamides, waxes, epoxy polymers, ethylene-acrylic acid copolymers, and ethylene-vinyl acetate copolymers, wherein each of said film-forming binder and said powdered thermoplastic polymer melts in the range of from about 65°C to about 180 degrees Celsius, (iii) a film forming binder selected from the group consisting of ethylene-acrylic acid copolymers, polyolefins, and waxes and which melts in the range of from about 65°C to about 180 degrees Celsius, (iv) a thermoplastic polymer selected from the group consisting of polyolefins, polyesters, and ethylene-vinyl acetate copolymers and which melts in the range of from about 65 to about 180 degrees Celsius or, (v) a thermoplastic polymer selected from the group consisting of polyolefins, polyesters, and ethylene-vinyl acetate copolymers, ethylene-methacrylic acid copolymers, and ethylene-acrylic acid copolymers and which melts in the range of from about 65 to about 180 degrees Celsius, wherein said transfer layer is capable of transferring and adhering developed image and non-image areas from said front surface of said support upon the application of heat energy to the rear surface of the support, said transfer layer strips from said front surface of the support by liquefying and releasing from said support when heated, said liquefied transfer layer providing adherence to a receptor element by flowing onto said receptor element and solidifying thereon, said adherence does not require an external surface adhesive layer and said transfer layer

The polyester layer can be formulated using any polyester or polyester polymer blends. Preferably, the polyester layer can include polyacrylates, polyacrylic acid, polymethacrylates, polyvinyl acetates, and co-polymer blends of vinyl acetate and ethylene/acrylic acid co-polymers.

The polyester layer is preferably prepared from, for example, a coating composition comprising an acrylic dispersion, an elastomeric emulsion, a plasticizer, and a water



repellant. The water repellant may comprise, for example, a polyurethane dispersion for the purpose of providing water resistance for a retention aid. The plasticizer may be, for example, polyethylene glycol. The polyester layer may further contain performance additives, such as polymers which are not esterified. Preferably, these include polyamide, polyimide or polyurethane polymer components.

Without being bound by any theory, upon back surface heating of the support, the polyester layer would undergo a solid to solution phase transition resulting in a transfer to the receptor of the polyester layer and any additional layers upon contact with a receptor. Edge to edge adhesion to the receptor occurs upon cooling of the release layer onto the receptor.

Upon cooling, an image receiving layer is transferred onto the receptor by removing the support/barrier layer. If the coatings are still hot upon removal, this is known as a "hot peel" product. If the coatings are at room temperature upon removal, the product is known as a "cold peel" product. If the coatings are at a temperature above room temperature but below the transfer temperature, the product is a "warm peel" product. The polyester layer of the present invention protects any transferred image, provides mechanical and thermal stability, as well as washability, preferably without losing the flexibility of the textile. The polyester layer should also provide a colorfast image (e.g. washproof) when transferred to the receptor surface. Thus, upon washing the receptor element (e.g. t-shirt), the image should remain intact on the receptor.

Further, the polyester layer satisfies the requirement for compatible components, in that the component dispersions remain in their finely dispersed state after admixture without coagulating or forming clumps or aggregated particles which would adversely affect image quality. Additionally, the polyester layer is preferably non-yellowing.

The polyester layer has a low content of organic solvents, and any small amounts present during the coating process are sufficiently low so as to meet environmental and health requirements. More specifically, the polyester layer preferably has a content of organic solvents of less than 2 % by weight of components. More preferably, the release layer has a content of organic solvents of less than 1% by weight of components.

Various additives may be incorporated into the polyester layer or the barrier and/or dye sublimation ink layers. Retention aids, wetting agents, plasticizers and water repellants are examples. Each will be discussed in turn below.

#### Retention Aids

5       An additive may be incorporated for the purpose of aiding in the binding of the applied colorant such as water-based ink jet colorants. Such additives are generally referred to as retention aids, and include polyamides, polyamines, polymer lactams, polymers and copolymers including pyrrolidone and/or imidazole. Retention aids that have been found to bind colorants generally fall into three classes: silicas, latex polymer and  
10   polymer retention aids. Silicas and silicates are employed when the colorant is water-based such as ink jet formulations. An example of widely used silicas are the Ludox (DuPont) brands. Polyvinyl alcohol represents a class of polymers that have also been applied to the binding of ink jet dyes. Other polymers used include anionic polymers such as Hercobond 2000 (Hercules). Reten 204LS (Hercules) and Kymene 736 (Hercules) are  
15   cationic amine polymer-epichlorohydrin adducts used as retention aids. Latex polymers include, by way of illustration, vinyl polymers and vinyl co-polymer blends such as ethylene-vinyl acetate, styrene-butadiene copolymers, polyacrylate and other polyacrylate-vinyl copolymer blends. The retention aids are present in an amount of from 0.1 to 40% by weight, preferably 0.1 to 20%, more preferably from 0.1 to 10%.

20

#### Wetting Agents and Rheology Modifiers

Wetting agents, rheology modifiers and surfactants may also be included in the polyester layer. Such agents may either be nonionic, cationic or anionic. The surfactant selected should be compatible with the class of polymers used in a formulation. For  
25   example, anionic polymers require the use of anionic or non-ionic wetting agents or surfactants. Likewise, cationic surfactants are stable in polymer solution containing cationic or non-ionic polymers. Examples of surfactants or wetting agents include, by way of illustration, alkylammonium salts of polycarboxylic acid, salts of unsaturated polyamine amides, derivatives of nonoxynol, derivatives of octoxynols (Triton X-100 and  
30   Triton X-114 (Union Carbide), for example), dimethicone copolymers, silicone glycol

copolymers, polysiloxane-polyether copolymers, alkyl polyoxy carboxylates, tall oil fatty acids, ethylene oxide-propylene oxide block copolymers and derivatives of polyethylene glycol. The wetting agents are present in an amount of from 0.1 to 40% by weight, preferably 0.1 to 20%, more preferably from 0.1 to 10%.

5 Viscosity modifiers may also be included. Generally, various molecular weight polyethylene glycols are incorporated to serve this purpose. Polyethylene glycols used generally range in molecular weight from 100 to 500,000 with molecular weights between 200 and 1000 being the most useful in this application.

## 10 Plasticizers

Plasticizers may be included in order to soften hard polymer and polymer blend additions. Plasticizers used include, by way of illustration, aromatic derivatives such as dioctyl phthalate, di-decyl phthalate derivatives and tri-2-ethylhexyl trimellitate. Aliphatic plasticizers include derivatives of ethylhexyl adipates and ethylhexyl sebacates.

15    Epoxidized linseed or soya oils may also be incorporated but generally are not used due to yellowing and chemical instability upon heat application. The plasticizers are present in an amount of from 0.1 to 40% by weight, preferably 0.1 to 20%, more preferably from 0.1 to 10%.

## Water Repellants

Water repellent aids may also be incorporated into order to improve the wash/wear resistance of the image. Examples of additives include polyurethanes, wax dispersions such as carnauba wax, mineral waxes, montan wax, derivatives of montan wax, petroleum waxes, synthetic waxes such as polyethylene and oxidized polyethylene waxes, hydrocarbon resins, amorphous fluoropolymers and polysiloxane derivatives. The water repellants are present in an amount of from 0.1 to 40% by weight, preferably 0.1 to 20%, more preferably from 0.1 to 10%.

Particularly when the imaging method is a laser printer or copier, the release layer of the present invention preferably excludes wax dispersions derived from, for example, a group including but not limited to natural waxes such as carnauba wax, mineral waxes, 30 montan wax, derivatives of montan wax, petroleum waxes, and synthetic waxes such as

polyethylene and oxidized polyethylene waxes. If the imaging method used is a non-laser printer/copier method it is not necessary to preferably exclude waxes from use in the transfer material. However, the amount of waxes that may be present in the transfer material of the invention when intended for use in laser printers or copiers must be  
5 sufficiently low as to avoid adverse affects on copier or printer operation. That is, the amount of wax present must not cause melting in the printer or copier.

The acrylic dispersion is present in a sufficient amount so as to provide adhesion of the polyester layer and image to the receptor element and is preferably present in an amount of from 46 to 90 weight %, more preferably 70 to 90 weight % based on the total  
10 composition of the polyester layer.

The elastomeric emulsion provides the elastomeric properties such as mechanical stability, flexibility and stretchability, and is preferably present in an amount of from 1 to 45 weight %, more preferably 1 to 20 weight % based on the total composition of the polyester layer.

15 The water repellant provides water resistance and repellency, which enhances the wear resistance and washability of the image on the receptor, and is preferably present in an amount of from 1 to 7 weight %, more preferably 3 to 6 weight % based on the total composition of the polyester layer.

The plasticizer provides plasticity and antistatic properties to the transferred image,  
20 and is preferably present in an amount of from 1 to 8 weight %, more preferably 2 to 7 weight % based on the total composition of the polyester layer.

Preferably, the acrylic dispersion is an ethylene acrylic acid co-polymer dispersion that is a film-forming binder that provides the "release" or "separation" from the support. The polyester layer of the invention may utilize the film-forming binders of the image-receptive  
25 melt-transfer film layer of U.S. Patent 5,242,739, which is herein incorporated by reference.

Thus, the nature of the film-forming binder is not known to be critical. That is, any film-forming binder can be employed so long as it meets the criteria specified herein. As a practical matter, water-dispersible ethylene-acrylic acid copolymers have been found to be especially effective film forming binders.

The term "melts" and variations thereof are used herein only in a qualitative sense and are not meant to refer to any particular test procedure. Reference herein to a melting temperature or range is meant only to indicate an approximate temperature or range at which a polymer or binder melts and flows under the conditions of a melt-transfer process to result in a substantially smooth film.

Manufacturers' published data regarding the melt behavior of polymers or binders correlate with the melting requirements described herein. It should be noted, however, that either a true melting point or a softening point may be given, depending on the nature of the material. For example, materials such as polyolefins and waxes, being composed mainly of linear polymeric molecules, generally melt over a relatively narrow temperature range since they are somewhat crystalline below the melting point.

Melting points, if not provided by the manufacturer, are readily determined by known methods such as differential scanning calorimetry. Many polymers, and especially copolymers, are amorphous because of branching in the polymer chains or the side-chain constituents. These materials begin to soften and flow more gradually as the temperature is increased. It is believed that the ring and ball softening point of such materials, as determined by ASTM E-28, is useful in predicting their behavior. Moreover, the melting points or softening points described are better indicators of performance than the chemical nature of the polymer or binder.

Representative binders (i.e., acrylic dispersions) for release from the support are as follows:

#### Binder A

Binder A is Michem® 58035, supplied by Michelman, Inc., Cincinnati, Ohio. This is a 35 percent solids dispersion of Allied Chemical's AC 580, which is approximately 10 percent acrylic acid and 90 percent ethylene. The polymer reportedly has a softening point of 102°C and a Brookfield viscosity of 0.65 pas (650 centipoise) at 140°C.

#### Binder B

This binder is Michem® Prime 4983R (Michelman, Inc., Cincinnati, Ohio). The binder is a 25 percent solids dispersion of Primacor® 5983 made by Dow Chemical Company. The polymer contains 20 percent acrylic acid and 80 percent ethylene. The

copolymer has a Vicat softening point of 43°C and a ring and ball softening point of 100°C. The melt index of the copolymer is 500 g/10 minutes (determined in accordance with ASTM D-1238).

#### Binder C

5        Binder C is Michem® 4990 (Michelman, Inc., Cincinnati, Ohio). The material is 35 percent solids dispersion of Primacor® 5990 made by Dow Chemical Company. Primacor® 5990 is a copolymer of 20 percent acrylic acid and 80 percent ethylene. It is similar to Primacor® 5983 (see Binder B), except that the ring and ball softening point is 93°C. The copolymer has a melt index of 1,300 g/10 minutes and Vicat softening point of  
10    39°C.

#### Binder D

This binder is Michem® 37140, a 40 percent solids dispersion of a Hoechst-Celanese high density polyethylene. The polymer is reported to have a melting point of 100°C.

#### 15        Binder E

This binder is Michem® 32535 which is an emulsion of Allied Chemical Company's AC-325, a high density polyethylene. The melting point of the polymer is about 138°C. Michem® 32535 is supplied by Michelman, Inc., Cincinnati, Ohio.

#### Binder F

20        Binder F is Michem® 48040, an emulsion of an Eastman Chemical Company microcrystalline wax having a melting point of 88°C. The supplier is Michelman, Inc., Cincinnati, Ohio.

#### Binder G

25        Binder G is Michem® 73635M, an emulsion of an oxidized ethylene-based polymer. The melting point of the polymer is about 96°C. The hardness is about 4-6 Shore-D. The material is supplied by Michelman Inc., Cincinnati, Ohio.

The second component of Polyester Layer Formulation 1 is an elastomeric emulsion, preferably a latex, and is compatible with the other components, and formulated to provide durability, mechanical stability, and a degree of softness and conformability to  
30    the layers.

Films of this material must have moisture resistance, low tack, durability, flexibility and softness, but with relative toughness and tensile strength. Further, the material should have inherent heat and light stability. The latex can be heat sensitized, and the elastomer can be self-crosslinking or used with compatible cross-linking agents, or  
5 both. The latex should be sprayable, or roll stable for continuous runnability on nip rollers.

Elastomeric latexes of the preferred type are produced from the materials and processes set forth in U.S. Patents 4,956,434 and 5,143,971, which are herein incorporated by reference. This curable latex is derived from a major amount of acrylate monomers such as C<sub>4</sub> to C<sub>8</sub> alkyl acrylate, preferably n-butyl acrylate, up to about 20 parts per hundred of total  
10 monomers of a monolefinically unsaturated dicarboxylic acid, most preferably itaconic acid, a small amount of crosslinking agent, preferably N-methyl acrylamide, and optionally another monolefinic monomer.

Using a modified semibatch process in which preferably the itaconic acid is fully charged initially to the reactor with the remaining monomers added over time, a latex of  
15 unique polymer architecture or morphology is created, leading to the unique rubbery properties of the cured films produced therefrom.

The third ingredient of Polyester Layer Formulation 1 is a water resistant aid such as a polyurethane dispersion which provides a self-crosslinking solvent and emulsifier-free aqueous dispersion of an aliphatic urethane-acrylic hybrid polymer which, alone, produces a  
20 clear, crack-free film on drying having very good scratch, abrasion and chemical resistance. This ingredient is also a softener for the acrylic dispersion and plasticizer aid.

Such product may be produced by polymerizing one or more acrylate and other ethylenic monomers in the presence of an oligourethane to prepare oligourethane acrylate copolymers. The oligourethane is preferably prepared from diols and diisocyanates, the  
25 aliphatic or alicyclic based diisocyanates being preferred, with lesser amounts, if any, of aromatic diisocyanates, to avoid components which contribute to yellowing. Polymerizable monomers, in addition to the usual acrylate and methacrylate esters of aliphatic monoalcohols and styrene, further include monomers with carboxyl groups, such as acrylic acid or methacrylic acid, and those with other hydrophilic groups such as the hydroxyalkyl acrylates  
30 (hydroxyethyl methacrylate being exemplary). The hydrophilic groups in these monomers

render the copolymer product dispersible in water with the aid of a neutralizing agent for the carboxyl groups, such as dimethylethanolamine, used in amount to at least partially neutralize the carboxyl groups after dispersion in water and vacuum distillation to remove any solvents used to prepare the urethane acrylic hybrid. Further formulations may include the addition of crosslinking components such as amino resins or blocked polyisocyanates. Although pigments and fillers could be added to any of the coating layers, such use to uniformly tint or color the coated paper could be used for special effect, but would not be used where an image is desired in the absence of background coloration. Urethane acrylic hybrid polymers are further described in U.S. 5,708,072, and their description in this application is incorporated by reference.

Self crosslinking acrylic polyurethane hybrid compositions can also be prepared by the processes and materials of U.S. 5,691,425, herein incorporated by reference. These are prepared by producing polyurethane macromonomers containing acid groups and lateral vinyl groups, optionally terminal vinyl groups, and hydroxyl, urethane, thiourethane and/or urea groups. Polymerization of these macromonomers produces acrylic polyurethane hybrids which can be dispersed in water and combined with crosslinking agents for solvent-free coating compositions.

Autocrosslinkable polyurethane-vinyl polymers are discussed in detail in 5,623,016 and U.S. 5,571,861, and their disclosure of these materials is incorporated by reference. The products usually are polyurethane-acrylic hybrids, but with self-crosslinking functions. These may be carboxylic acid containing, neutralized with, e.g. tertiary amines such as ethanolamine, and form useful adhesives and coatings from aqueous dispersion.

The elastomeric emulsion and polyurethane dispersion are, generally, thermoplastic elastomers. Thermoplastic elastomeric polymers are polymer blends and alloys which have both the properties of thermoplastic polymers, such as having melt flow and flow characteristics, and elastomers, which are typically polymers which cannot melt and flow due to covalent chemical crosslinking (vulcanization). Thermoplastic elastomers are generally synthesized using two or more monomers that are incompatible; for example, styrene and butadiene. By building long runs of polybutadiene with intermittent polystyrene runs, microdomains are established which imparts the elastomeric quality to the polymer system.



However, since the microdomains are established through physical crosslinking mechanisms, they can be broken by application of added energy, such as heat from a hand iron, and caused to melt and flow; and therefore, are elastomers with thermoplastic quality.

Thermoplastic elastomers have been incorporated into the present invention in order to provide the image system with elastomeric quality. Two thermoplastic elastomer systems have been introduced; that is, a polyacrylate terpolymer elastomer (for example, Hystretch V-29) and an aliphatic urethane acryl hybrid (for example, Daotan VTW 1265). Thermoplastic elastomers can be chosen from a group that includes, for example, ether-ester, olefinic, polyether, polyester and styrenic thermoplastic polymer systems. Specific examples include, by way of illustration, thermoplastic elastomers such as polybutadiene, polybutadiene derivatives, polyurethane, polyurethane derivatives, styrene-butadiene, styrene-butadiene-styrene, acrylonitrile-butadiene, acrylonitrile-butadiene-styrene, acrylonitrile-ethylene-styrene, polyacrylates, polychloroprene, ethylene-vinyl acetate and poly (vinyl chloride). Generally, thermoplastic elastomers can be selected from a group having a glass transition temperature (T<sub>g</sub>) ranging from about -50°C to about 25°C.

The fourth component of Polyester Layer Formulation 1 is a plasticizer such as a polyethylene glycol dispersion which provides mechanical stability, water repellency, and allows for a uniform, crack-free film. Accordingly, a reason to add the polyethylene glycol dispersion is an aid in the coating process. Further, the polyethylene glycol dispersion acts as an softening agent. A preferred fourth component is Carbowax Polyethylene Glycol 400, available from Union Carbide.

An optional fifth ingredient of Polyester Layer Formulation 1 is a surfactant and wetting agent such as polyethylene glycol mono ((tetramethylbutyl) phenol) ether. In another embodiment of the invention, the polyester layer comprises an acrylic binder and a wax emulsion. The polyester layer may further contain a retention aid such as Hercobond 2000<sup>®</sup>. The retention aid provides water resistance, which enhances the washability of the image on the support. In another embodiment of the invention, the polyester layer described in Polyester Layer Formulation 2 is divided into two separate layers. An example of this embodiment is a layer comprising ethylene acrylic acid that allows release or separation. An elastomer and polyurethane of the present invention, as

well as any additives discussed above, are combined in a second layer that provides the above-described transfer qualities (i.e., washability).

An additional embodiment of the present invention is a transfer sheet comprising, as the polyester layer, the third layer of U.S. Patent No. 5,798,179 to Kronzer (US '179).

- 5 That is, the polyester layer may comprise a thermoplastic polymer which melts in a range of from about 65°C to about 180°C and has a solubility parameter less than about 19 (Mpa)<sup>1/2</sup>.

- The third layer in U.S. '179 functions as a transfer coating to improve the adhesion of subsequent layers in order to prevent premature delamination of the heat transfer  
10 material. The layer may be formed by applying a coating of a film-forming binder over the second layer. The binder may include a powdered thermoplastic polymer, in which case the third layer will include from about 15 to about 80 percent by weight of a film-forming binder and from about 85 to about 20 percent by weight of the powdered thermoplastic polymer. In general, each of the film-forming binder and the powdered thermoplastic  
15 polymer will melt in a range from about 65°C to about 180°C. For example, each of the film-forming binder and powdered thermoplastic polymer may melt in a range from about 80°C to about 120°C. In addition, the powdered thermoplastic polymer will consist of particles which are from about 2 to about 50 micrometers in diameter.

- Polyester Layer Formulation 1 is a preferred embodiment of the invention. In  
20 another embodiment of the invention (Polyester Layer Formulation 2), the polyester layer comprises an acrylic binder and a wax emulsion. The polyester layer may further contain a retention aid such as Hercobond 2000®. The retention aid provides water resistance, which enhances the washability of the image on the receptor.

- In another embodiment of the invention, the release layer of U.S. application  
25 09/541,083 filed March 31, 2000 to Williams et al. may be used in the present invention.

- In another embodiment of the invention, the above-described polyester layer is divided into two separate layers. An example of this embodiment is a layer comprising ethylene acrylic acid that allows release or separation. An elastomer and polyurethane of the present invention, as well as any additives discussed above, are combined in a second  
30 layer that provides the above-described transfer qualities (i.e., washability).

Preferably, the polyester layer is applied by using gravure, cascade, metered rod, fountain or air knife coating methods.

B. Receptor Element

5           The receptor or receiving element receives the transferred image. A suitable receptor includes but is not limited to textiles including 100 % cotton fabric, and cotton blend fabric, such as a cotton/polyester blend fabric. The receptor element may also include glass, canvas, metal, wool, plastic, ceramic or any other suitable receptor. Preferably the receptor element is a tee shirt or the like.

10           The image, as defined herein, may be applied in any desired manner, and is preferably applied using offset printing.

To transfer the image, a support layer coated with a barrier layer is imaged by using sublimation dyes, then the polyester layer is coated onto the imaged coated support layer to form a transfer sheet. The transfer sheet is then placed on the receptor element, with the polyester layer in contact with the receptor element. Energy is applied to the rear surface of the transfer sheet to transfer the image and polyester layer to the receptor element. Preferably, the energy applied is heat energy. The heat energy can be applied using a heating device (i.e., a hand iron or heat press). The temperature range of the hand iron is generally in the range of 110 to 220°C with about 190°C being the preferred temperature. The heat press operates at a temperature range of 100 to 220°C with about 190°C being the preferred temperature. The heating device is placed over the non-image side of the transfer sheet and moved, for instance, in a circular motion (hand iron only). Pressure (i.e., typical pressure applied during ironing) must be applied as the heating device is moved over the transfer sheet. After about two minutes to five minutes (with about three minutes being preferred) using a hand iron or 10 seconds to 50 seconds using a heat press (with about twenty seconds being preferred) of heat and pressure, the heating device is removed from the transfer sheet. The transfer sheet is optionally allowed to cool from one to five minutes. The support and barrier layer are then peeled away from the image which is imbedded in the polyester layer which is adhered to the receptor.

The following examples are provided for a further understanding of the invention, however, the invention is not to be construed as limited thereto.

The following table can be used as a guide to determine optimum coating weights and thickness of the Barrier, Polyester and Image Layers:

Coat Weights and Thickness				
	Parts	Wet Coat (g/m <sup>2</sup> )	Dry Coat (g/m <sup>2</sup> )	Thickness (mil)
Barrier Layer	50	28	2 to 20	0.05 to 0.80
Release Layer	95	96.2	12 to 50	0.48 to 2.00
Image Layer	100	20	2 to 25	0.1 to 3.5

5

In a preferred embodiment of the invention, the barrier layer is a vinyl acetate polymer. An example of this embodiment is Barrier Layer Formulation 1:

#### Barrier Layer Formulation 1

<u>Components</u>	<u>Parts</u>
Polyvinyl acetate-dibutyl maleate co-polymer dispersion (such as EVERFLEX G, Hampshire Chemical Corporation)	50 parts
Water	50 parts

10

Barrier Layer Formulation 1 may be prepared as follows: fifty parts of a vinyl acetate-dibutyl maleate polymer dispersion are combined with fifty parts of water by gentle stirring. The stirring is continued for approximately ten minutes at a moderate stir rate (up to but not exceeding a rate where cavitation occurs.). The amount of water added may vary.

15 The only limitation is that sufficient water is added to make the dispersion coatable on the support.

#### EXAMPLE 2

In another embodiment of the present invention, the barrier layer contains a polyester resin such as polymethyl methacrylate (PMMA) in a molecular weight range of from 15,000

to 120,000 Daltons. An example of the PMAA-containing barrier layer is Barrier Layer Formulation 2:

**Barrier Layer Formulation 2**

<u>Components</u>	<u>Parts</u>
Acetone 99.5%	40 parts (weight)
2-Propanol 99.5%	40 parts (weight)
PMMA	20 parts (weight)

5

Barrier Layer Formulation 2 may be prepared as follows: The acetone and 2-propanol are weighed and mixed, and the mixture is stirred. One half of the PMMA is added to the mixture while the mixture is heated to about 25°C and stirring continues until the PMMA is dispersed. At this point, stirring continues until the remainder of the PMMA is  
10 added to the mixture and is dispersed. The mixture is then allowed to cool to room temperature.

EXAMPLE 3

Another example of the barrier layer of the present invention is Barrier Layer Formulation 3:

Compound	Chemical Class	General (parts by mass)	Preferably (parts by mass)	Most Preferably (parts by mass)
Uvacure 1500 <sup>a</sup>	Cycloaliphatic epoxide	10.0-60.0	20.0-50.0	30.0-40.0
Uvacure 1562 <sup>b</sup>	cycloaliphatic epoxy resin	40.0-0.0	30.0-10.0	25.0-15.0
DEN 431 <sup>c</sup>	epoxy novolac resin	5.0-30.0	10.0-20.0	12.0-18.0
2-propanol	Alcohol	44.4-0.0	38.3-12.4	30.8-21.7
Uvacure 1590 <sup>a</sup>	activated epoxy	0.5-7.0	1.5-6.0	2.0-4.0
Ebecryl BPO <sup>a</sup>	aryl ketone	0.1-1.0	0.2-0.6	0.2-0.5
BYK 354 <sup>c</sup>	Polyacrylate	0.0-1.0	0.0-0.5	0.0-0.4
BYK 088 <sup>c</sup>	Polysiloxane	0.0-1.0	0.0-0.5	0.0-0.4

<sup>a</sup>UCB Chemical Corporation - Radcure Business Unit

<sup>b</sup>Dow Chemicals

<sup>c</sup>BYK Chemie

Barrier Layer Formulation 3 is prepared as follows: DEN 431, an extremely  
5 viscous material, is placed into a beaker first, followed by 2-propanol. The remaining  
compounds are added in the order in which they appear listed in the table. Manual  
agitation may be required especially because of the extreme viscosity of DEN 431. Once  
mechanical agitation is used, the mixture is stirred for about 30-60 minutes at a rate just  
below the point where cavitation would have occurred.

10

#### EXAMPLE 4

A barrier layer comprising Barrier Layer Formulation 3 is cured as follows: a thin  
film of barrier layer formulation 1, in the range of 1.0 g/m<sup>2</sup> to 20 g/m<sup>2</sup>, is applied to a  
support and cured at <50 mJ/cm<sup>2</sup> with a mercury vapor ultraviolet lamp.

EXAMPLE 5

Example 4 is repeated, and after UV curing, the film is further cured at temperatures between 60°C and 200° in a heat chamber for 1 to 45 minutes.

5

EXAMPLE 6

In one embodiment of the invention, the polyester layer comprises an ethylene acrylic acid co-polymer dispersion, an elastomeric emulsion, and a polyurethane dispersion. An example of this embodiment is Polyester Layer Formulation 1:

**Polyester Layer Formulation 1**

10

<u>Components</u>	<u>Parts by weight</u>
Ethylene Acrylic Acid Co-polymer Dispersion (Michem Prime 4983R, Michelman)	86 parts
Elastomeric emulsion (Hystretch V-29, BFGoodrich)	5 parts
Polyurethane dispersion (Daotan VTW 1265, Vianova Resins)	4 parts
Polyethylene Glycol (Carbowax Polyethylene Glycol 400, Union Carbide)	4 parts
Polyethylene Glycol Mono ((Tetramethylbutyl) Phenol) Ether (Triton X-100, Union Carbide)	1 part

Polyester Layer Formulation 1 may be prepared as follows: five parts of the elastomer dispersion are combined with eighty-six parts of an ethylene acrylic acid co-polymers dispersion by gentle stirring to avoid cavitation. Four parts of a polyurethane dispersion are then added to the mixture. Immediately following the addition of a polyurethane dispersion, four parts of a polyethylene glycol and one part of an nonionic surfactant (e.g., Triton X-100) are added. The entire mixture is allowed to stir for

15

approximately fifteen minutes at a moderate stir rate (up to but not exceeding a rate where cavitation occurs). Once thoroughly combined, the mixture is filtered (for example, through a 53  $\mu$ m nylon mesh).

5

#### EXAMPLE 7

Another embodiment may be found in Polyester Layer Formulation 2:

#### **Polyester layer Formulation 2**

	Components	Parts by weight
10	Ethylene Acrylic Acid Co-polymers dispersion (Michem Prime 4938R, Michelman)	74 parts
	Wax Dispersion (Michelman 73635M, Michelman)	25 parts
15	Retention Aid (Hercobond 2000, Hercules)	1 part

Alternatively, the binders suitable for Polyester Layer Formulation 1 may be used in lieu of the above-described ethylene acrylic acid copolymer dispersion.

20 Formulation 2 may be prepared in the following manner: the ethylene acrylic acid co-polymer dispersion and the wax dispersion are stirred (for example in a beaker with a stirring bar). The retention aid is added, and the stirring continues until the retention aid is completely dispersed.

25

#### EXAMPLE 8

#### Conventional Offset Printed Dye Sublimation Transfer

A paper support is coated with a barrier layer of Barrier Layer Formulation 1. The coated support is then printed, image-wise, using a dye sublimation four to eight color ink set. A four color dye sublimation ink set is preferred. Once printed, the paper support,



barrier layer and printed image are then coated with the polyester layer of Polyester Layer Formulation 1.

The polyester layer is coated using gravure coating methods. Once coated, the image is transferred to 100% cotton fabric through the application of heat energy using  
5 either a hand iron or heat press on the rear surface of the support. The transferred image is allowed to cool. The paper support and barrier layer are stripped away from the transferred image.

#### EXAMPLE 9

A film support is coated with a barrier layer of Barrier Layer Formulation 2. The  
10 coated support is then printed using screen printing. Once printed, the film support, barrier layer and printed image are then coated with the polyester layer of Polyester Layer Formulation 2.

The polyester layer is coated using cascade coating methods. Once coated, the image is transferred to 100% cotton fabric through the application of heat energy using  
15 either a hand iron or heat press on the rear surface of the support. The transferred image is allowed to cool to a warm temperature. The film support and barrier layer are stripped away from the transferred image.

#### EXAMPLE 10

20 A film support is coated with a barrier layer of Barrier Layer Formulation 3. The coated support is then printed using screen printing. Once printed, the film support, barrier layer and printed image are then coated with the polyester layer of Polyester Layer Formulation 2.

The polyester layer is coated using cascade coating methods. Once coated, the  
25 image is transferred to 100% cotton fabric through the application of heat energy using either a hand iron or heat press on the rear surface of the support. The transferred image is allowed to cool to a warm temperature. The film support and barrier layer are stripped away from the transferred image.

### EXAMPLE 11

A film support is coated with a barrier layer of Barrier Layer which is a 1gsm-15gsm coating of 100% Evcote PWR-25™ (EvCo Co.) which is a PET polymer (polyethylene phthalate polymer derivative) and is thermosetting. The coated support is  
5 then printed using screen printing. Once printed, the film support, barrier layer and printed image are then coated with the polyester layer of Polyester Layer Formulation 2.

The polyester layer is coated using cascade coating methods. Once coated, the image is transferred to 100% cotton fabric through the application of heat energy using either a hand iron or heat press on the rear surface of the support. The transferred image is  
10 allowed to cool to a warm temperature. The film support and barrier layer are stripped away from the transferred image.

### EXAMPLE 12

A paper support is coated with a barrier layer of Barrier Layer Formulation 1. The  
15 coated support is then printed, image-wise, using a dye sublimation set of: Disperse Black (Bafixan Black; BASF); Disperse Blue (Bafixan Blue; BASF); Disperse Yellow (Bafixan Yellow; BASF); Disperse Red (Bafixan Red; BASF). Once printed, the paper support, barrier layer and printed image are then coated with the polyester layer of Polyester Layer Formulation 1.

20 The polyester layer is coated using gravure coating methods. Once coated, the image is transferred to 100% cotton fabric through the application of heat energy using either a hand iron or heat press on the rear surface of the support. The transferred image is allowed to cool. The paper support and barrier layer are stripped away from the transferred image.

25

### EXAMPLE 13

A paper support is coated with a barrier layer of Barrier Layer Formulation 1. The coated support is then printed, image-wise, using a dye sublimation Offset set of medium energy inks: Dye HT Subli Cyan, Magenta and Yellow Inks from Superior Ink, Inc. Once

printed, the paper support, barrier layer and printed image are then coated with the polyester layer of Polyester Layer Formulation 1.

The polyester layer is coated using gravure coating methods. Once coated, the image is transferred to 100% cotton fabric through the application of heat energy using  
5 either a hand iron or heat press on the rear surface of the support. The transferred image is allowed to cool. The paper support and barrier layer are stripped away from the transferred image.

#### EXAMPLE 14

10 This Example demonstrates the image transfer procedure. Referring to Figure 1, to transfer the image, (1) the substrate 20 coated with the barrier layer 40 is imaged 50, and the image is coated with a polyester layer 5. The imaged substrate is placed with the polyester layer 5 against a receptor 30 of the present invention. Accordingly, the receptor 30 of this example includes but is not limited to cotton fabric, cotton blend fabric, glass  
15 and ceramic. A transfer device of the present invention (i.e., a hand iron or heat press) is used to apply heat to the substrate 20 and barrier layer 40, which in turn releases the image 10 and polyester layer 5. The temperature transfer range of the hand iron is about 190°C. The heat press operates at a temperature transfer range of about 190°C. (2) The transfer device is placed over the non-image side of the substrate 20 and moved in a circular  
20 motion (if the hand iron is used). Usual pressure applied when ironing is applied as the heating device is moved over the substrate 20. After about 180 seconds (15 seconds if using the heat press) of heat and pressure, the transfer device is removed from the substrate 20. The substrate 20 and barrier layer 40 are allowed to cool for about five minutes. (3) The substrate 20 and barrier layer 40 are then peeled away from the receptor.  
25

#### EXAMPLE 15

Referring to Figure 2, the method of applying an image to a receptor element will be described. More specifically, Figure 1 illustrates how the step of heat transfer from the transfer sheet 50 to a tee shirt or fabric 62 is performed.

The transfer sheet is prepared, and imaged upon as described in the Examples 8 and 9. A tee shirt 62 is laid flat, as illustrated, on an appropriate support surface, and the imaged surface of the transfer sheet 50 is positioned onto the tee shirt. An iron 64 set at its highest heat setting is run and pressed across the back 52A of the transfer sheet. The  
5 image and non-image areas are transferred to the tee shirt and the transfer sheet is removed and discarded.

All cited patents, publications, copending applications, and provisional applications referred to in this application are herein incorporated by reference.

10 The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the present invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

1 We claim:

1 1. A method for producing a transfer sheet, which comprises the steps of:

2 (i) imaging a transfer sheet with sublimation dyes, wherein said transfer sheet  
3 comprises:

4 a support having a first and second surface, and

5 a barrier layer having a first and second surface, wherein the first surface of said  
6 barrier layer is applied to the first surface of said support, and wherein a sublimation dye  
7 image is applied to the second surface of said barrier layer; and

8 (ii) applying a first surface of a polyester layer, having a first and second  
9 surface, to said sublimation dye image applied to the second surface of said barrier layer,  
10 provided that the polyester layer does not comprise thermosetting materials.

1 2. A method of applying a sublimation dye image to a receptor element, which  
2 comprises, in the following order, the steps of:

3 (i) imaging a transfer sheet with sublimation dyes, wherein said transfer sheet  
4 comprises:

5 a support having a first and second surface, and

6 a barrier layer having a first and second surface, wherein the first surface of said  
7 barrier layer is applied to the first surface of said support, and wherein said sublimation  
8 dye image is applied to the second surface of said barrier layer;

9 (ii) applying a first surface of a polyester layer, having a first and second  
10 surface, to said image applied to the second surface of said barrier layer to produce a  
11 transfer sheet, provided that the polyester layer does not comprise thermosetting materials;

12 (iii) positioning the second surface of said polyester layer against said receptor  
13 element;

14 (iv) applying heat energy to the rear surface of the transfer sheet to transfer said  
15 sublimation dye image and said polyester layer to said receptor element, wherein said  
16 sublimation dyes sublimate and penetrate into said polyester layer adhered to said receptor  
17 element; and

18 (v) stripping said transfer sheet away from said receptor element, wherein the  
19 sublimation dye image-containing polyester layer is adhered to said receptor element.

1 3. The method of claim 1 or 2, wherein said imaging is provided by ink jet, offset,  
2 gravure, flexographic, laser or screen printing.

1 4. The method of claim 1 or 2, wherein said support is selected from the group  
2 consisting of a paper support, a film support and cellulosic nonwoven webs.

1 5. The method of claim 4, wherein said film support comprises a polyester.

1 6. The method of claim 1 or 2, wherein said sublimation dyes are a four to eight  
2 color dye sublimation ink set.

1 7. The method of claim 1 or 2, wherein the polyester layer is applied by using  
2 gravure, cascade, metered rod, fountain or air knife coating methods.

1 8. The method of claim 8, wherein the heat energy is applied using a hand iron or  
2 a heat press.

1 9. The method of claim 2, wherein the receptor element is 100% cotton fabric or a  
2 cotton/polyester blend fabric.

1 10. The method of claim 2, wherein the receptor element is selected from the  
2 group consisting of ceramic, glass, wood, plastic and metal surfaces.

1 11. The method of claim 1 or 2, wherein the barrier layer comprises a polymer  
2 dispersion.

1           12. The method of claim 11, wherein the polymer dispersion comprises one or  
2 more of the components selected from the group consisting of polyacrylates, styrene-  
3 butadiene copolymers, ethylene-vinyl acetate copolymers, nitrile rubbers,  
4 poly(vinylchloride), poly(vinylacetate) and ethylene-acrylate copolymers.

1           13. The method of claim 12, wherein the polymer dispersion comprises polyvinyl  
2 acetate dibutyl maleate copolymer.

1           14. The method of claim 1 or 2, wherein said polyester layer comprises a (a)  
2 polyester or polyester/copolymer blend, (b) an elastomeric emulsion, (c) a water repellant  
3 and (d) a plasticizer, wherein the polyester or polyester/polymer blend melts in the range  
4 of about 60°C to 270°C.

1           15. The method of claim 14, wherein said polyester or polyester/polymer blend is  
2 selected from the group consisting of polyacrylates, polyacrylic acid, polymethacrylates,  
3 polyvinyl acetates, copolymer blends of vinyl acetate and ethylene/acrylic acid  
4 copolymers.

1           16. The method of claim 14, wherein the polyester layer further comprises  
2 performance additives.

1           17. The method of claim 14, wherein said water repellant is a polyurethane  
2 dispersion and said plasticizer is polyethylene glycol.

1           18.     A transfer sheet having a first and second surface, comprising  
2           (i)       a support layer having a first and second surface,  
3           (ii)      a barrier layer applied to the second surface of said support layer,  
4           (iii)     a dye sublimation ink-containing layer applied to said barrier layer, and

- 5 (iv) a polyester layer applied to said dye sublimation ink-containing layer,  
6 provided that the polyester layer does not contain thermosetting  
7 materials.

1 19. A method of transferring an sublimation dye image to a receptor element  
2 comprising:

- 3 (i) providing a transfer sheet having a front and a back surface, which  
4 comprises, in the following order, the layers:  
5 (a) a support,  
6 (b) a barrier layer,  
7 (c) a dye sublimation ink-containing layer, and  
8 (d) a polyester layer, provided the polyester layer does not contain  
9 thermosetting materials;  
10 (ii) positioning the front surface of said transfer sheet against a receptor  
11 element;  
12 (iii) applying heat energy to the rear surface of the transfer sheet to transfer  
13 said sublimation dye image to said receptor element, wherein said  
14 sublimation dyes sublime and penetrate into said polyester layer  
15 adhered to said receptor element; and  
16 (iv) stripping said transfer sheet away from said receptor element, wherein  
17 the sublimation dye image-containing polyester layer is embedded in  
18 said receptor element.

1 20. A kit comprising at least one transfer sheet according to claim 18.

1 21. A kit according to claim 20, further comprising a receptor element.

1 22. A kit comprising:

- 2 (i) a support layer having a first and second surface,  
3 (ii) a barrier layer applied to the second surface of said support layer,



- 4           (iii)     a marking agent containing at least one sublimation dye,
- 5           (iv)     a polyester material to be applied to said marking agent, provided that
- 6                     the polyester layer does not contain thermosetting materials.

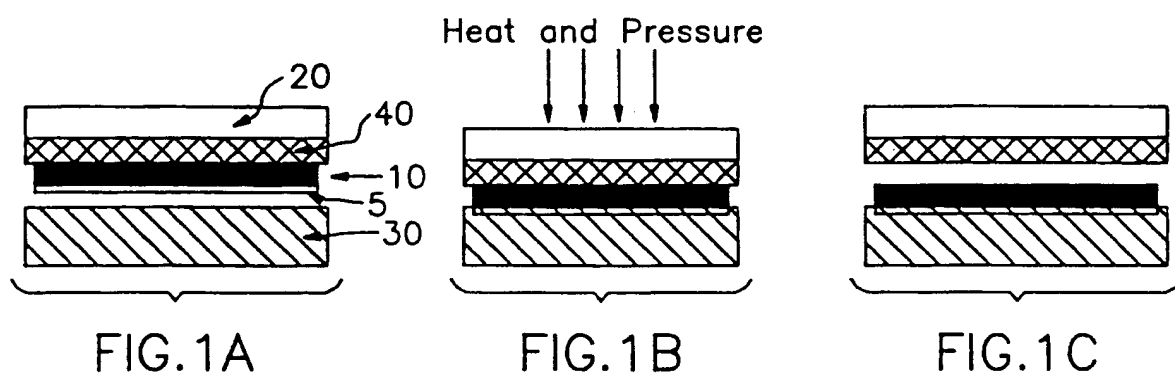
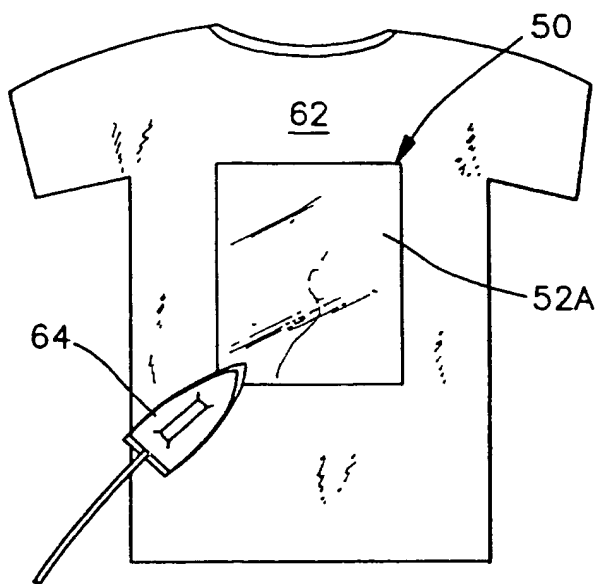


FIG. 2



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/26796

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D06P5/00 B41M5/035 D06Q1/12 B44C1/17

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06P B41M D06Q B44C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 741 387 A (COLEMAN KENNETH R) 21 April 1998 (1998-04-21) cited in the application column 6, line 16 -column 7, line 4; claims	1-12, 18-22
Y	EP 0 351 085 A (BRANDYWINE MOTIFS LTD) 17 January 1990 (1990-01-17) the whole document	1-12, 18-22
A	GB 2 084 931 A (HELIOME LTD) 21 April 1982 (1982-04-21) the whole document	1-22
A	GB 2 147 614 A (PORTER KENNETH) 15 May 1985 (1985-05-15) the whole document	1-22

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 December 2000

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# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 00/26796

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5741387	A	21-04-1998	NONE	
EP 0351085	A	17-01-1990	DK 311689 A GB 2220008 A,B PT 90954 A,B	25-12-1989 28-12-1989 29-12-1989
GB 2084931	A	21-04-1982	NONE	
GB 2147614	A	15-05-1985	NONE	